Tempearture Dependence on Mutual Solubility Data of the Binary (Methanol a-Pinene or b-Pinene) Systems and Ternary Liquid-Liquid Equilibria for the (Methanol Ethanol a-Pinene or b-Pinene) Systems.

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Temperature dependence on mutual solubility of binary (methanol + limonene) mixture and liquid-liquid equilibria of ternary (methanol + ethanol + limonene) mixture

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Abstract

Mutual solubility data of the binary (methanol + limonene) mixture at the temperatures ranging from 288.15 K close to upper critical solution temperature, and ternary liquid-liquid equilibria (tie-lines) of the (methanol + ethanol + limonene) mixture at the temperatures 288.15 K, 298.15 K and 308.15 K have been measured. The experimental results have been represented accurately in terms of the extended and modified UNIQUAC models with binary parameters, compared with the UNIQUAC model. The temperature dependence of binary and ternary liquid-liquid equilibria for the binary (methanol + limonene) and ternary (methanol + ethanol + limonene) mixtures could be calculated successfully using the extended and modified UNIQUAC model.

Keywords: Liquid + liquid equilibria (LLE), Limonene, Alcohol, UNIQUAC model

1. Introduction

Limonene is used lately as a eco-friendly solvent for cleaning and removal of oil from machine parts and for volume reduction and recycling of polystyrene by dissolving into formed polystyrene as a novel application. Limonene is a kind of monoterpene ($C_{10}H_{16}$) available from fresh peel of citrus fruits such as lemon and grapefruit and is readily soluble in hydrocarbons and alcohols except for methanol, and partially miscible in methanol and water. We have been studied the mutual solubilities of terpenes (α-pinene, β-pinene, and limonene) and the multicomponent liquid-liquid equilibria of terpene mixtures with alcohol and/or water at the temperature 298.15 K. So far the mutual solubility and liquid-liquid equilibria of terpene mixtures were reported: (water + methanol + terpene) [1], (water + ethanol + terpenes) [2], (water + terpenes + 1-propanol or butanol) [3], (water + ethanol + limonene, or citral) [4, 5]. In a previous paper, the mutual solubility of the system (α-pinene, β-pinene + methanol) and the liquid-liquid equilibria of the ternary mixtures of (α-pinene, β-pinene + methanol) with ethanol were examined at the temperature range from 288.15 K to 308.15 K. [6]. Based on the oleophilic effect of the -CH2- group of alcohols to terpenes, which acts in favour of the increasing miscibility of terpenes with increasing number of methylene groups of alcohols, it is interesting to explain that the partial miscibility of the binary mixture (methanol + terpenes) is compared to the full miscibility of (ethanol + terpenes) or + 1-propanol and + 1-butanol. Besides, the difference between the miscibility and immiscibility of the ternary mixture (methanol + ethanol + terpenes) is characterized by the hydrophilic-lipophilic balance to terpenes in hydrogen bonding of methanol and ethanol.

In the present work, we continue to measure the mutual solubility data of the binary system (methanol + limonene) at temperatures ranging from 288.15 K close to an upper critical solution temperature and the liquid-liquid equilibria (tie-lines) for the ternary (methanol + ethanol + limonene) mixture at the temperatures T = 288.15 K, 298.15 K and 308.15 K. Additionally we examine the temperature dependence on the mutual solubility data and the ternary liquid-liquid equilibria for these mixtures using the original UNIQUAC, [7] the extended UNIQUAC [8] and the modified UNIQUAC [9] models.

2. Experimental section

2.1 Materials

Purities of the chemicals used in this work were in their mass percent as follow: (+)-limonene (Fluka, abbreviated as limonene, ≥ 99%; methanol (Wako), ≥ 99.7%; and ethanol (Wako), ≥ 99.5%. All chemicals were used without further purification. Densities of chemicals were measured with an Anton Paar (DMA58) densimeter at 298.15K, and compared with the literature values [10] as shown in Table 1.

2.2 Experimental procedure and results

Liquid-liquid equilibrium (LLE) measurements for the ternary (methanol + ethanol + limonene) mixture were carried out at the temperatures T = 288.15 K, 298.15 K and 308.15 K, and the binary (methanol + limonene) system were measured at temperatures ranging from 288.15 K close to upper critical solution temperature and at atmospheric pressure. As details of the experimental apparatus and procedures were previously described elsewhere [11], the feature descriptions are given as follows. The mixtures loaded in an equilibrium cell were stirred vigorously by using a magnetic stirrer for 5 h, and settled for 5 h enough to separate two phases. The separation time needed to form an equilibrium biphase

was verified by a preliminary measurement. After phase equilibrium has been reached, samples of two layers were withdrawn with a precision Hamilton syringe and their compositions were analyzed by a GLC (Shimadzu, GC-8A) equipped with a thermal conductivity detector. The temperatures of injection port and detector were set at 513 K and the oven temperature was increased from 403 K to 513 K at a rate of 32 K/min. The helium flow rates for both the separation and reference columns were set at 50 ml/min. A stainless steel column packed with Porapak Q with 2 m in length was used to separate every component. The peak area of the components, detected to analyze with a chromatopac (Shimadzu, C-R6A), was calibrated by gravimetrically weighed mixtures. For each sample solution, three analyses were made to obtain a mean value. The accuracy of the tie-line measurements was estimated to be within ± 0.001 in mole fraction.

Tables 2 and 3 summarize the experimental LLE tie-line compositions for the binary (methanol + limonene) mixture, and the ternary (methanol + ethanol + limonene) mixture, respectively. The ternary LLE of the (methanol + ethanol + limonene) system consist of two miscible systems (methanol + ethanol) and (ethanol + limonene), and one immiscible system (methanol + limonene), whose phase behavior showed a type I according to the classification of Sørensen and Arlt [12].

3. Calculated results and discussion

Liquid-liquid equilibrium (LLE) calculations were performed by solving the thermodynamic criteria and mass balance equation.

$$(f_i x_i)^I = (f_i x_i)^{II} \tag{1}$$

$$\sum_i x_i^I = \sum_i x_i^{II} = 1 \tag{2}$$

where *I* and *II* represent equilibrium phases and x is the liquid-phase mole fraction and f the activity coefficient.

To represent the experimental binary and ternary LLE results, we used three kinds of activity coefficient models; the original UNIQUAC, [7] the extended UNIQUAC [8] and the modified UNIQUAC [9]. In the extended and modified UNIQUAC models, the interaction correction factor of pure component q' was used to improve the phase equilibrium representation. The molecular-geometric volume and surface parameters of pure component, r_i and q_i, estimated from the Bondi's method [13], and the correlation factor q'_i, taken from the references [8, 9, 14, 15], were listed in Table 4. In the modified UNIQUAC model [9], which couples with the combinatorial correction term of Gmehling et al. [16] and the residual term of the extended UNIQUAC model involving a universal value of the third parameter C. The adjustable binary parameters τ_{ij} is defined in terms of the binary energy parameters a_{ij}

$$\tau_{ij} = \exp\left(-\frac{a_{ij}}{CT}\right) \tag{3}$$

which C was set to 0.65 [9].

3.1 Results of mutual solubilities for (methanol + limonene) system

In the binary LLE correlations, the adjustable energy parameters of binary (methanol + limonene) mixture were obtained using the experimental compositions from 288.15 K to upper critical solution

temperatures by solving equations (1) and (2) at every temperature. The energy parameters were assumed to be given by a quadratic function of temperature, because the linear temperature dependence of the energy parameters could not yield quantitative agreement with experimental data.

$$a_{ij} = A_{ij} + B_{ij}T + C_{ij}T^2 \tag{4}$$

The coefficients A_{ij}, B_{ij}, and C_{ij} of the energy parameter a_{ij} were obtained fitting by a least square minimization method, and listed in Table 5. Figure 1 (a) shows the experimental mutual solubilities for (methanol + limonene) system and the values calculated by the modified UNIQUAC model. The coexistence curves having an upper critical solution temperature can be satisfactorily described by the modified model as the mutual solubilities are coming to be miscible completely as the system temperature goes up to the critical solution point. The experimental results measured at 298.15 K shown in Figure 1 (a) were in good agreement with the values reported prevously. The binary parameters at each temperature estimated by the modified UNIQUAC model were in good agreement with the results calculated by equation (4) as shown in Figure 1 (b).

3.2 Results of ternary LLE for (methanol + ethanol + limonene) system

The ternary LLE of the (methanol + ethanol + limonene) system consists of two miscible systems (methanol + ethanol) and (ethanol + limonene), and one immiscible system (methanol + limonene). In the representation of the ternary LLE, the binary energy parameters of the miscible mixture (methanol + ethanol) [14] can be obtained from binary experimental vapour-liquid equilibria using the thermodynamic equations:

$$py_i\phi_i = x_i f_i p_i^* \phi_i^* \exp\{v_i^L (p - p_i^*)/RT\} \tag{5}$$

$$\ln\phi_i = (2\sum_j y_j B_{ij} - \sum_i \sum_j y_i y_j B_{ij})\, p/RT \tag{6}$$

where x is the liquid-phase mole fraction and y the vapour-phase mole fraction, p the total pressure, f the activity coefficient, ϕ the fugacity coefficient, and ϕ^* the fugacity coefficient at p^* were calculated by equation (5). The pure and cross second virial coefficient B_{ij} in equation (6) were estimated by the method of Hayden and O'Connell [17]. The pure component vapour pressure p^* was calculated by using the Antoine equation with coefficients taken from the literature [14]. The liquid molar volume v^L was obtained by a modified Racket equation [18]. An optimum set of the binary energy parameters a_{ij} was obtained using a maximum-likely-hood principle [19], where standard deviations in the measured quantities were set as σ_p = 133 Pa for pressure; σ_T = 0.05 K for temperature; σ_x = 0.001 for liquid mole fraction; σ_y = 0.003 for vapour mole fraction. Table 6 summarizes the binary parameters and calculated results for constituent binary systems.

As no binary VLE data for the miscible (ethanol + limonene) mixture can be available from the literature, the binary parameters for the (ethanol + limonene) system were obtained fitting the models to the experimental ternary LLE (methanol + ethanol + limonene) system by minimizing the following objective function by means of the simplex method [20].

$$F = 100\left\{\sum_k^n \sum_i^3 \sum_j^2 \left(x_{ijk}^{exp} - x_{ijk}^{cal}\right)^2 \Big/ 6N\right\}^{0.5} \tag{7}$$

where N denotes tie-lines k =1 to N, phases j = 1 and 2, components i = 1, 2, and 3. Table 7 lists the correlated binary parameters of the (ethanol + limonene) system and root mean square deviations (RMS) between the experimental and calculated results by three models. The mean deviations correlated for the ternary system at 288.15, 298.15 and 308.15 K calculated by equation (7) were 1.05 mol %, 0.89 mol % and 0.59 mol % for the UNIQUAC model, extended and modified UNIQUAC models, respectively. The modified UNIQUAC model could reproduce accurately the experimental results in comparison with other two models. Figure 2 compares the experimental tie-line data and ternary LLE results of the (methanol + ethanol + limonene) system at 288.15, 298.15 and 308.15 K with those correlated in terms of modified UNIQUAC model. As shown in Figure 2, the temperature dependence of the ternary LLE envelopes could be represented successfully by the modified UNIQUAC model.

3.3 Distribution ratio of ethanol in the ternary system

The distribution of ethanol (component 2) in the ternary LLE mixture is defined by the ratio of mole fraction of ethanol in methanol-rich phase to that in limonene rich-phase.

$$D = x_2^{methanol\ phase} \Big/ x_2^{limonene\ phase} \tag{8}$$

Figure 3 shows the distribution ratio of ethanol for the ternary (methanol + ethanol + limonene) mixture at T = 288.15 K, 298.15 K and 308.15 K. The experimental results were compared with those calculated by the modified UNIQUAC model and fair agreement between the experimental values and calculated ones was obtained. Limonene acts as the increasing miscibility with increasing number of methylene groups of alcohols. From Figure 3, it is found that ethanol in limonene phase is distributed greater than that of methanol phase due to the oleophilic effect of the -CH2- group of ethanol to limonene in comparison with methanol.

4. Conclusions

Mutual solubility data of the binary system (methanol + limonene) at temperatures ranging from 288.15 K close to upper critical solution temperature and liquid-liquid equilibria (tie-lines) for the ternary (methanol + ethanol + limonene) mixture at T = 288.15 K, 298.15 K and 308.15 K were measured. The experimental mutual solubility data and ternary liquid-liquid equilibrium data have been calculated accurately using the modified UNIQUAC models within the experimental uncertainties. The temperature dependence of binary and ternary liquid-liquid equilibria for the binary (methanol + limonene) and ternary (methanol + ethanol + limonene) mixture could be representated accurately using the modified UNIQUAC model.

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TABLE 1

Densities of pure components at $T = 298.15$K

Component	Exp. ρ/g·cm^{-3}	Lit.[a] ρ/g·cm^{-3}
(+)-Limonene	0.83731	0.83840
Methanol	0.78662	0.78637
Ethanol	0.78524	0.78493

[a] Reference [10].

TABLE 2

Mutual solubility data of methanol (1) + limonene (2) system at different temperatures

T/K	Methanol rich phase	Limonene rich phase
	x_1	x_1
288.15	0.9062	0.2076
293.30	0.8957	0.2317
298.15	0.8819	0.2769
302.94	0.8626	0.3128
308.15	0.8381	0.3839
312.14	0.8115	0.4712
313.37	0.7889	0.5473

TABLE 3

Ternary liquid-liquid equilibrium data of methanol (1) + ethanol (2) + limonene (3) mixture at T = 288.15, 298.15 and 308.15 K

Methanol rich phase		Limonene rich phase	
x_1	x_2	x_1	x_2
	288.15K		
0.8452	0.0422	0.2256	0.0152
0.7784	0.0882	0.2484	0.0318
0.7176	0.1239	0.2705	0.0557
0.6271	0.1333	0.3720	0.0841
0.5923	0.1403	0.4002	0.1010
	298.15K		
0.8534	0.0271	0.2715	0.0082
0.8261	0.0429	0.2844	0.0168
0.7480	0.0728	0.3422	0.0362
0.6301	0.1097	0.4508	0.0758
	308.15K		
0.8182	0.0099	0.4105	0.0053
0.7840	0.0217	0.4330	0.0132
0.7741	0.0234	0.4524	0.0157
0.7560	0.0247	0.4719	0.0235

TABLE 4

Structural parameters for pure components

Component	r [a]	q [a]	q' [b]	q' [c]
(+)-Limonene	6.278	5.208	$q^{0.2}$	$q^{0.75}$
Methanol	1.430	1.430	1.000	1.482
Ethanol	2.110	1.972	1.000	1.404

[a] References [14, 15].

[b] Reference [8].

[c] Reference [9].

TABLE 5

Constants A, B and C of binary parameter a_{ji} used in modified UNIQUAC model

System (1 + 2)	A_{12} A_{21}	B_{12} /K B_{21} /K	10^{-3} C_{12} /K^2 $10^{-3}C_{12}$ /K^2
Methanol + limonene	-430.088	4.18660	-8.715
	-329.675	12.2907	-25.50

$$a_{ij} = A_{ij} + B_{ij}T + C_{ij}T^2$$

TABLE 6

Calculated results of binary vapour-liquid and liquid-liquid equilibrium data reduction

System(1+2)	T/K	N	model	a_{12}/K	a_{21}/K	δP/kPa	δT/K	$10^3\delta x$	$10^3\delta y$	ref
Methanol + ethanol	298.15	11	I	-141.75	169.45	0.18			0.7	14[a]
			II	262.72	-118.69	0.56	0.01	0.3	3.0	
			III	292.63	-132.64	0.57	0.01	0.3	3.0	
Methanol + limonene	288.15	MS	I	-5.0490	604.01					
			II	373.50	1282.4					
			III	52.672	1094.6					
	298.15	MS	I	-7.4991	585.37					
			II	369.47	1265.2					
			III	43.442	1068.0					
	308.15	MS	I	-10.266	562.35					
			II	362.56	1242.2					
			III	32.469	1036.3					

N, number of data points. MS, mutual solubility.

I, UNIQUAC; II, Extended UNIQUAC; III, Modified UNIQUAC.

[a] Binary energy parameters and deviations were taken from ref. [14].

TABLE 7

Calculated results for ternary system methanol(1) + ethanol(2) + limonene(3)

T/K	N	Model	RMS /mol %	Binary parameters	
				a_{23}/K	a_{32}/K
288.15	6	I	1.64	-162.44	302.57
		II	1.38	166.53	1089.5
		III	0.75	-5.4976	1253.1
298.15	5	I	1.17	-157.29	279.72
		II	1.07	176.49	1088.0
		III	0.82	-2.9936	1133.7
308.15	5	I	0.36	-257.30	338.99
		II	0.21	160.14	998.43
		III	0.19	-45.771	879.81

I, UNIQUAC. II, Extended UNIQUAC. III, Modified UNIQUAC.

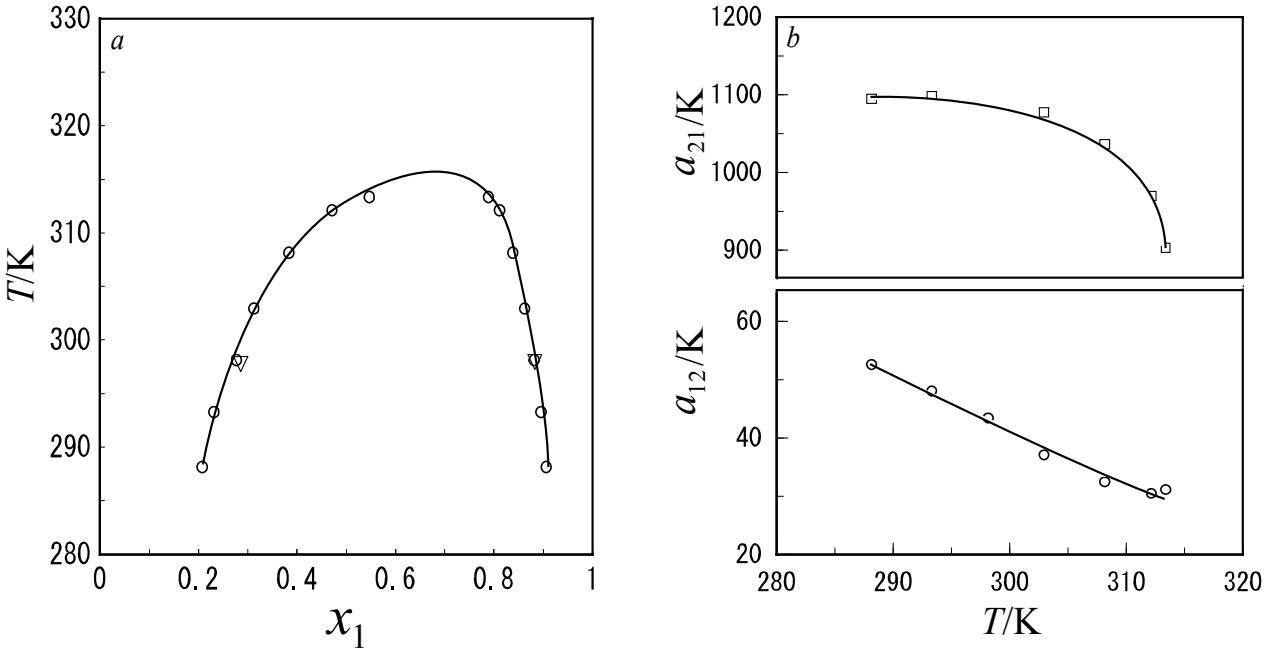

FIGURE 1. Experimental and calculated results for binary system (methanol + limonene). (*a*) (○), mutual solubility data; (▽), data at 298.15K from reference [1]; (———), calculated. (*b*) temperature dependence of binary energy parameters.

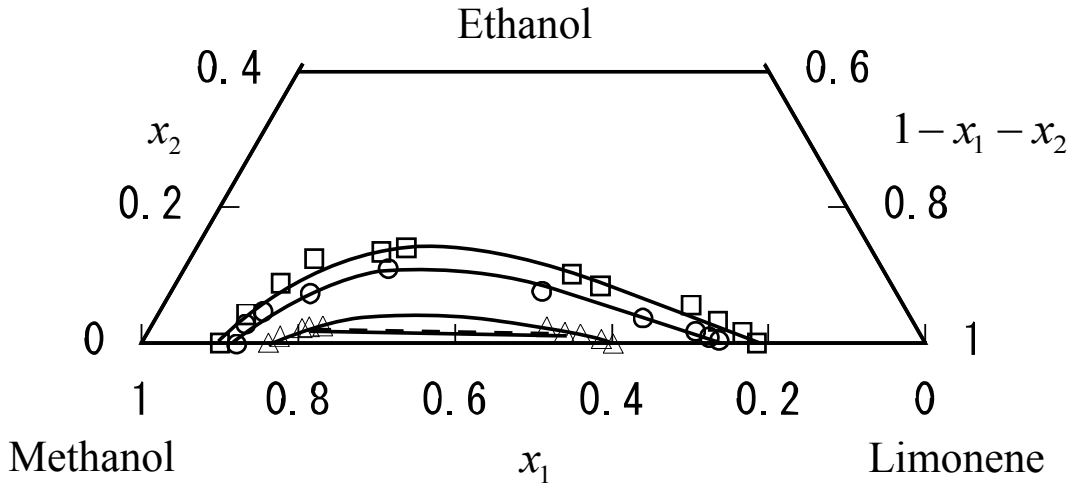

FIGURE 2. Liquid-liquid equilibrium data of the ternary systems (methanol + ethanol + limonene) at 288.15, 298.15 and 308.15K. Experimental data. (□), at 288.15K, (○), at 298.15K, and (△) and (- - - -), tie-line at 308.15K; (———), correlated by modified UNIQUAC model.

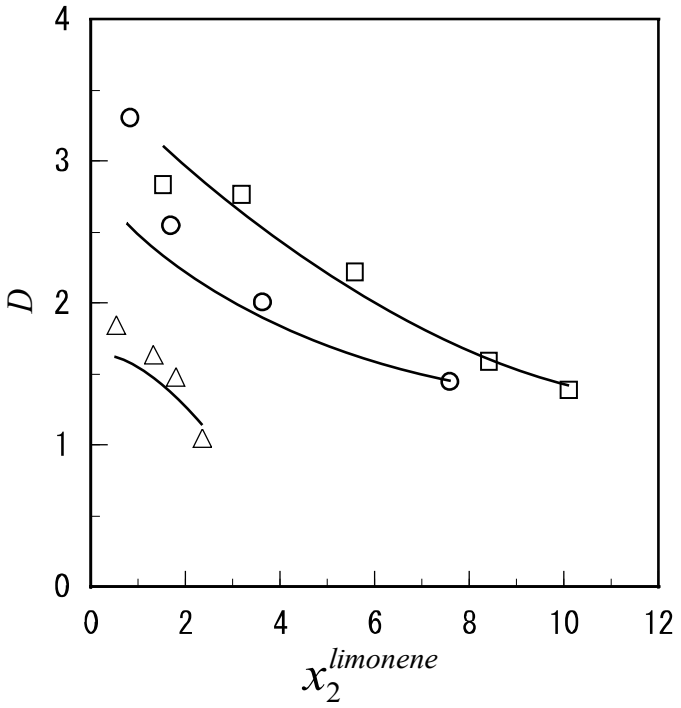

FIGURE 3. Distribution ratio of ethanol in limonene rich phase at 288.15, 298.15 and 308.15K. Experimental data. (□), at 288.15K, (○), at 298.15K, and (△), at 308.15K; (———), correlated by modified UNIQUAC model.